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"On the Atomic Weight of Glucinum (Beryllium)." Second Paper. By T. S. HUMPIDGE, Ph.D., B.Sc., Professor of Chemistry in the University College of Wales, Aberystwyth. Communicated by E. FRANKLAND, F.R.S. Received February 27, 1885. Read March 5.

In a former communication which I had the honour of making to the Royal Society,[*] I described a method of preparing metallic glucinum and of determining its specific heat. From my experiments I deduced the result that the atomic weight of the metal must be 13·6 (*circâ*) in order to agree with Dulong and Petit's rule.

It is well known that the position assigned to glucinum in the periodic arrangement of the elements requires an atomic weight of two-thirds the above number, or approximately 9, and that with the larger atomic weight it falls between carbon and nitrogen, and is entirely out of place.

Various criticisms were offered to explain this apparently anomalous result. To the suggestion of Professor J. E. Reynolds[†] that the pure metal would have a specific heat 50 per cent. greater than that of a sample containing 6 per cent. of impurities, I have already replied.[‡] Another explanation was offered by Brauner,[§] who thought it possible that the specific heat of the metal might increase with the temperature and thus agree with Dulong and Petit's rule, at some higher temperature-interval than 0—100°. Brauner's suggestion was based upon the position which glucinum should occupy in the periodic arrangement and which would be similar to that of boron and carbon. Some determinations of the specific heat of the metal up

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[*] "Phil. Trans.," 1883, Part II, p. 601.
[†] "Proc. Roy. Soc.," vol. 35, p. 248.
[‡] "Proc. Roy. Soc.," vol. 35, p. 358.
[§] "Berlin Ber.," xi, 872.

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to 300° made by Nilson and Petterson* confirmed this prediction to a certain extent, but as this important question could not be considered as definitely decided, the following investigations were undertaken. Owing to the small amount of time at my disposal the experiments have absorbed the greater part of my leisure for the past fourteen months, and in the mean time my results have been partly forestalled by other investigators, but the importance of the subject justifies me in publishing what is little more than a confirmation of the work of others.

My experiments may be divided into two groups, (i) those on the specific heat of pure glucinum at varying temperatures, and (ii) those on the vapour-density of volatile glucinum compounds.†

I. *Specific Heat of Metallic Glucinum at varying Temperatures.*

For the determinations of the specific heat of glucinum at varying temperatures a fresh quantity of the metal was prepared from the pure chloride by the method which I have previously described (*loc. cit.*). The chloride was obtained from oxide which had been carefully purified with ammonium carbonate. Experiments in which impure glucina was fused with acid potassium fluoride, and the fused mass extracted with water containing hydrofluoric acid, proved that if iron is present much of it goes into solution with the glucinum. The usual method with ammonium carbonate gives better results, especially if the process is several times repeated, and if at last an insufficient quantity of the solvent is used, so that some of the glucina remains undissolved with the last traces of the alumina. The concentrated solution of the double carbonate‡ can then be easily decomposed by leading steam into it through a wide tube. The dangerous bumping which always happens when the concentrated solution is boiled is thus completely avoided. In this way, after three or four purifications, it is easy to obtain a sample of glucina which when fused with acid potassium fluoride dissolves in water containing hydrofluoric acid without leaving the slightest trace. A very convenient form of charcoal for mixing with the oxide to prepare the chloride is a kind of lamp-black known in trade as *gas-black*. When burnt it leaves a much smaller quantity of ash than the best sugar charcoal, and can be mixed with the oxide much more easily and intimately than the latter.

Most of the metallic glucinum prepared from this pure chloride was in the form of thin, lustrous, highly crystalline laminæ. The purer portions were selected and compressed in a steel mortar to a compact, lustrous cylinder 11 mm. long and 8 mm. in diameter.

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* "Berlin Ber.," xiii, 1456.

† The latter experiments were done before the former.

‡ See Appendix A.

An analysis of a portion of this metal after the specific heat determinations had been done was conducted as follows. Since aluminium was absent in the oxide and could not have been introduced during the preparation of the metal, the only impurities to be looked for were silicon, iron, and glucinum oxide. On solution of the metal in a dilute acid, the silicon would mostly remain behind in the free state, but a part would be liberated as silicon hydride.* The oxide would also remain undissolved as the metal had been heated up to 450° in the specific heat determinations. The iron would, of course, dissolve.

29·4 mgrms. of the metal was dissolved in dilute sulphuric acid, and left a minute, imponderable residue, which was estimated at 0·2 mgrm. It remained floating in the liquid for some time, was light coloured, and was probably glucina mixed with some ferric oxide. The iron in solution was estimated by the depth of colour produced by ammonium sulphocyanate, just as by the operation known as "Nesslerising" minute quantities of ammonia are estimated. I believe this method gives more accurate results for the estimation of very small quantities of iron than the usual process with potassium permanganate. In using a dilute solution of this reagent a considerable excess must be added before the pink colour becomes visible, and the end point or amount of excess is very difficult to determine; whereas with ammonium sulphocyanate and working under similar conditions it is very easy to match the two colours and to determine accurately a minute quantity of iron. The iron in the above solution of glucinum sulphate was oxidised by a drop of weak bromine-water, the excess of bromine boiled off, and a given volume of ammonium sulphocyanate added in a Nessler cylinder. To another similar cylinder, containing the same quantity of free acid and ammonium sulphocyanate and made up to the same volume, was added a solution of ferric sulphate containing 0·1 mgrm. iron per c.c. Of this solution 0·3 c.c. was required, corresponding to 0·03 mgrm. iron. The composition of the metal was therefore :—

Glucinum	99·20
Glucina	0·70
Iron	0·10
	100·00

in other words, it was almost pure. Its purity was also shown by the difficulty with which it dissolved in dilute acids. A small piece which had been left in dilute sulphuric acid (1 : 10) over night was only partly dissolved in the morning, but solution took place rapidly on warming.

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* The silicon in commercial magnesium behaves in this manner.

Several attempts were made to determine the density of this block of metal. They were all unsuccessful, owing to the difficulty of completely removing the enclosed air.

Another sample was therefore used in the loose form as extracted from the iron boats. The following results were obtained :—

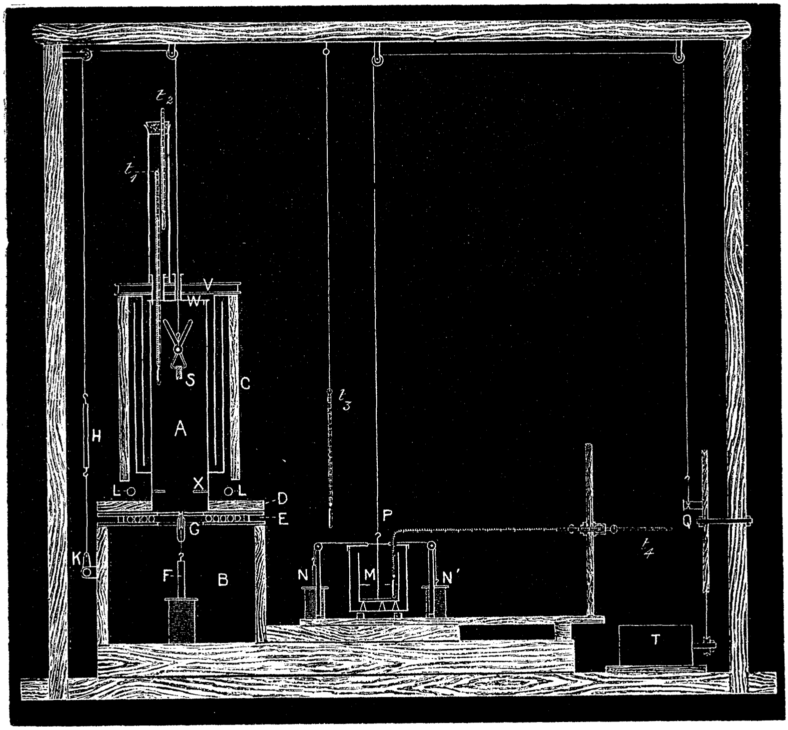
$$d\tfrac{20}{20} = 1\cdot88 \text{ (i)},\ 1\cdot90 \text{ (ii)};\ \text{mean} = 1\cdot89.$$

The composition of this metal was—

Gl	99·00
GlO..............	0·43
Fe	0·57
	100·00

and making allowance for these impurities the true density of glucinum becomes $d\tfrac{20}{20} = 1\cdot85$.

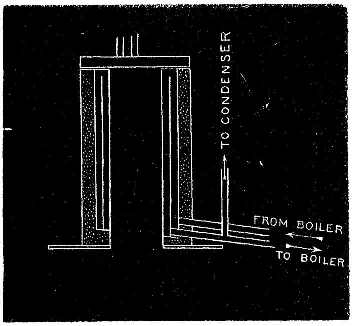
Fig. 1.



Owing to the small amount of substance used (about 59 mgrms.), the result is only accurate to the second decimal place.

The calorimeter employed was an improved form of the instrument described in my former paper (*loc. cit.*). The opening and closing of the two sliders, and the movement of the catch to release the substance, were, however, made automatic by suitable electrical connexions. It was thus only necessary to run the calorimeter under the heater and back again in order to transfer the substance from the latter to the former. The calorimeter (M, fig. 1), with its brass casing, and the bent thermometer (t_4), were the same as those used before; the agitator (P) was worked by a small electromotor (T). Two new heaters were used, one for temperatures up to 150°, and one for temperatures from 150° to 300°. The former (fig. 2) consists of a double brass vessel with a thick jacket of slag-wool. The vapour of the boiling liquid passes from the boiler to the heater by one tube, and leaves by another, is condensed and flows back to the boiler. The liquids used in this heater were methyl alcohol, water, and xylol, but the results obtained with the first-named liquid were inaccurate owing to the small rise (0·6°) in the temperature of the calorimeter. In this apparatus it is possible to obtain a temperature constant to $\frac{1}{10}$° for any length of time.*

Fig. 2.



The heater for high temperatures (A, fig. 1) was made on the pattern described by Lothar Meyer†, the construction of which will be evident from the figure. C is an outer non-conducting casing, L is a ring burner, from which the heated gases pass up through the heater and escape through perforations in the double lid (V). This heater is mounted on a thick slab of asbestos (D), by means of which it stands on two brass plates (E), which are separated from one another by a coil of thin lead tubing, through which a current of cold water flows. In this way the chamber (B) into which the calorimeter has to be run is kept quite cool. A double tin screen (not shown in the figure) serves also to prevent the calorimeter from receiving extraneous heat. The whole operation of transferring the substance from the heater to the calorimeter can be performed in less than two seconds, and the gain of heat by the calorimeter during this period cannot be measured. In a series of blank experiments it was found that when the calorimeter remained under the heater (at 300°) for 15 seconds, the thermometer t_4 rose $\frac{1}{100}°$. The temperature of the substance in the heater was measured by three delicate thermometers from Geissler. Their fixed points were determined in ice, water, naphthalene, and benzophenone, but they were not calibrated. The gas supply for this heater was regulated by three regulators made by Giroud, of Paris, burning 60, 80, and 110 litres of gas per hour, and giving temperatures of 200°, 240°, and 310° respectively. With these regulators the temperature could be kept constant to about $\frac{1}{4}°$, provided there were no great fluctuations in the gas pressure. I have sadly felt the need of a good regulator for high temperatures.[*] The suspension of the substance (S) in the heater was by a small pair of tongs, made so that the jaws open when the arms are closed. The tongs with the substance are supported by a thin platinum wire which is attached, outside the heater, to a thread passing over pulleys and fastened to a catch (K). When this catch is released the tongs fall by their own weight until they reach the ring X; this brings the arms closer together, and the substance drops into the calorimeter. The connexions are so arranged that when the calorimeter is run under the heater, the lid of the calorimeter casing is first opened, then the slider under the heater, and finally the catch is released, and the substance falls. As the calorimeter returns the two sliders are again closed.

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* This is only true for a liquid with a constant boiling point; the xylol used had to be fractionated several times before a constant temperature could be obtained.

† "Berlin Ber.," xvi, 1087.

The liquid used in the calorimeter was purified turpentine, of which the specific was determined as follows:—

(i.) By the method of mixtures, using metallic magnesium, of which the specific had been found to be $c_{100}^{13}=0{\cdot}2442$. This gave for the turpentine $k_{10}=0{\cdot}4146$.[†]

(ii.) By Andrews' calorifier[‡] the mean of two series of experiments gave $k_{10}=0{\cdot}4103$.

(iii.) By Pfaundler's apparatus[§] (Joule's principle), in which equal weights of water and turpentine contained in two similar calorimeters are heated by two platinum wires of equal resistance, through which the same current passes. Three experiments gave the mean result, $k_{10}=0{\cdot}4085$.

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[*] I am much indebted to Professor L. Meyer for advice and assistance in the construction of these two heaters.

[†] For details of these and the following experiments, see Appendix C.

[‡] "Ann. Chim. et Phys." [3], xiv, 92.

[§] "Wien. Akad. Ber.," lix.

The general mean of these experiments is $k_{10}=0{\cdot}4112$.

The specific heat of water was taken as 1·0000 at 0°, and the correction for temperature used was that obtained by Münchhausen and Wüllner, and by Baumgartner and Pfaundler, viz., $k_t=1+0{\cdot}0003t$. Regnault's expression for the change in the specific heat of turpentine was employed, *i.e.*, $k_t=k_0+0{\cdot}00124t$, omitting the third term, which only inappreciably affects the results in the small range through which the liquid was heated.

The following table contains the results of the specific heat determinations of glucinum* made with this apparatus. Column I gives the results actually obtained; Column II these results corrected for the impurities contained in the metal:—

		I.	II.
Experiments 1 and 2	$c^{11}_{100} =$	0·4267	0·4286
,, 3 ,, 4	$c^{13}_{145} =$	0·4500	0·4515
,, 5 ,, 6	$c^{11}_{193} =$	0·4676	0·4696
,, 7 ,, 8	$c^{15}_{240} =$	0·4866	0·4885
,, 9 ,, 10	$c^{14}_{312} =$	0·5087	0·5105

These numbers show a rapid and continuous increase in the specific heat as the temperature rises. In order to find whether this increase continued above 300°, two experiments were made at higher temperatures with a double calorimeter. This calorimeter consisted of two thin brass vessels, placed close together with suitable thermometers and agitators. One of these received the glucinum, and the other a platinum cylinder of known weight. These two substances were placed in two similar glass tubes, packed side by side in a wide iron tube with slag-wool, and the whole heated in the furnace which was used for the vapour-density determinations.† After the heating had been continued for about three hours, the iron tube was withdrawn, and the substances quickly tipped into the calorimeters. In calculating the temperature, Violle's results of the specific heat of platinum at varying temperatures were used. These two experiments gave th following results:—

		I.	II.
Experiment 11	$c^{11}_{360} =$	0·5178	0·5199
,, 12	$c^{17}_{447} =$	0·5384	0·5403

which show that although the specific heat continues to increase, i does so more slowly than at lower temperatures.

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* The metal was enclosed in a platinum capsule, soldered air-tight with pure gold

† See Sequel.

The quantity of heat (Q_t) required to raise 1 gram of a substance from 0° to $t°$ can be expressed by the equation—

$$Q_t = kt + \alpha t^2 + \beta t^3,$$

where k is the true specific heat at 0°, and α and β are constants. From this equation the mean specific heat between any two temperatures (t' and t) is

$$c_{t'}^{t} = k + \alpha(t + t') + \beta(t^2 + tt' + t'^2).$$

The numerical values obtained for the three unknowns from the experimental values of $c_{t'}^{t}$ are

$$k = 0{\cdot}3756\,; \quad \alpha = 0{\cdot}00053\,; \quad \beta = -0{\cdot}00000038.$$

A comparison of the value for the mean specific heats calculated from the above expression with those obtained by direct experiment shows that the two agree within the experimental errors, and that this expression correctly represents the change in the specific heat of glucinum.

$t' : t$.	$c_{t'}^{t}$ found.	$c_{t'}^{t}$ calculated.
11° : 100°	0·4286	0·4302
13 : 145	0·4515	0·4505
11 : 193	0·4696	0·4687
15 : 240	0·4885	0·4875
14 : 312	0·5105	0·5097
11 : 360	0·5199	0·5215
17 : 447	0·5403	0·5425

The three constants being known, the true specific heat at any temperature (k_t) is found by making $t' = t$, and the above equation becomes

$$k_t = k + 2\alpha t + 3\beta t^2,$$

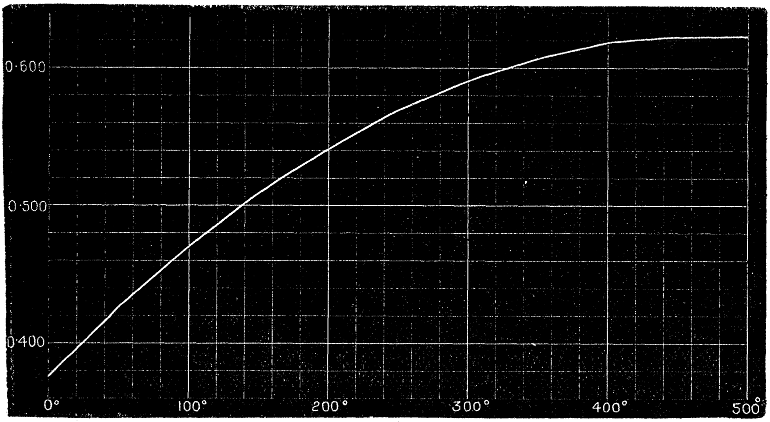
or with numerical values,

$$k_t = 0{\cdot}3756 + 0{\cdot}00106t - 0{\cdot}00000114t^2,$$

whence the following values for k_t may be calculated—

$$\begin{aligned} k_0 &= 0{\cdot}3756 \\ k_{100} &= 0{\cdot}4702 \\ k_{200} &= 0{\cdot}5420 \\ k_{300} &= 0{\cdot}5910 \\ k_{400} &= 0{\cdot}6172 \\ k_{500} &= 0{\cdot}6206 \end{aligned}$$

Fig. 3.



Curve showing specific heat of glucinum at varying temperatures.

A curve showing the true specific heat at varying temperatures is given in fig. 3. According to the above expression the specific heat reaches a maximum at about 470°, and then falls. But it is doubtful whether this expression would correctly represent the specific heat at temperatures above 500°. Weber's experiments with diamond and graphite tend to confirm this doubt. His results between $-79°$ and $+280°$ show a rapid increase in the specific heat, and give a parabolic curve similar to that obtained for glucinum. But in the other experiments which he made between 600° and 1000° the increase in the specific heat is much less rapid, and the curve takes another form. However this may be, my results show that the specific heat of glucinum rapidly increases up to about 400°, and that between 400° and 500° it remains practically constant at the approximate value of 0·62. If this number is multiplied by the atomic weight taken as 9·1, the atomic heat becomes 5·64. It is therefore clear that this number represents the true atomic weight, and not 13·6, as was previously deduced from the specific heat between 100° and 10°. Glucinum is thus to be classed with those elements of which the specific heat increases rapidly with the temperature, and, like most elements with low atomic weights, its atomic heat is considerably below the average.

The expression for the true specific heat of the metal given by Nilson's results is similar to that obtained from mine. His values for the constants, as calculated by me, are: $k_0 = 0·3710$, $\alpha = 0·00058$, and $\beta = -0·00000044$, which closely agree with those derived from my experiments.

II. *Vapour-density of Volatile Glucinum Compounds.*

The compounds of glucinum which can be volatilised unchanged are those which it forms with organic radicals and with the halogens. Of the former class Cahours states* that he has prepared the ethide and propide, and gives their boiling-points, but all my efforts to prepare either of these compounds in a sufficiently pure state to determine its vapour-density were fruitless. I operated, as Cahours recommends, on an excess of metallic glucinum with mercuric ethide or propide in sealed tubes; but either the tubes exploded violently, always when a temperature of 135° was exceeded, or if the change was successfully accomplished, as shown by the separation of metallic mercury, the compound decomposed again on distilling. Mercuric ethide acts on glucinum chloride, slowly at 100°, more rapidly at 130°, and a considerable quantity of mercury ethyl chloride is produced, which partly remains dissolved in the excess of mercuric ethide, and partly separates out in the usual pearly scales. A similar reaction takes place between mercuric ethide and glucinum bromide, but from neither of these reactions could a volatile compound of glucinum be obtained. I hope to be able to examine these interesting reactions at a later date.

As the organic compounds of glucinum were not available for vapour-density determinations, my attention was directed to the halogen compounds. The bromide, chloride, and iodide of glucinum are all volatile, and their volatility is in the order named. The first two volatilise without decomposition if water and air are absent; the last-named decomposes on heating. In the presence of a trace of air, both the chloride and bromide decompose when heated, the latter more easily than the former; in both cases the haloid element is set free. And since both these compounds corrode glass and porcelain when vaporised in vessels of these substances, the determination of their vapour-density is a matter of some difficulty.

I first made some determinations in glass tubes with the chloride, using Schwarz's modification† of V. Meyer's displacement method. The glass was corroded, and the results were not concordant. Porcelain was also attacked. The tubes nearly always contained free chlorine, although the experiments were done in pure dry nitrogen. It was then decided to try platinum for the determination, and after it had been found that glucinum chloride could be sublimed unchanged in a platinum tube in a stream of nitrogen, a platinum vessel was obtained from Messrs. Johnson, Matthey, and Co. This platinum vessel was of the usual size and dimensions of those employed for vapour-density determinations by displaced air, except that the narrow tube was about one-half the ordinary length. The open end of this tube was firmly attached to the upper part of the usual glass apparatus by well-wired caoutchouc tubing.* The substance was introduced, and the displaced air measured by the method used by Meier and Crafts† in their researches on the vapour-density of iodine. As a graduated vessel for the reception of the displaced air, an ordinary calibrated burette was used, the lower end being connected with a tube of the same width by strong caoutchouc tubing. These two tubes were held in common retort-stand clips, and could be easily adjusted, so that the mercury was at the same level in each. They were connected with the vessel in the furnace by a narrow glass tube (1 mm. bore), and the one containing the air was immersed in a vessel of water. As a furnace, two of Fletcher's draft furnaces were used, placed one above the other, with a wide clay cylinder between them. This gave a chamber 30 cm. high and 12·5 cm. in diameter, which could be heated up to any temperature from about 400° to 800°. The temperature could be kept sufficiently constant for these experiments with a good gas tap.

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* "Compt. rend.," lxxvi.

† "Berlin Ber.," xvi, 1051.

The obvious errors in this modification have been pointed out by V. Meyer ("Berlin Ber.," xvii, 1334). They are chiefly that a portion of the wide tube is irregularly heated, and that the large boat which carries the substance takes air with it in its fall into the tube.

The platinum vessel was freely suspended in two clay crucibles, placed mouth to mouth, and with a hole knocked in the bottom of the upper. This served to protect the vessel from the direct action of the furnace gases. The temperature was measured by a Siemens' pyrometer, the porcelain tube of which was connected with platinum wires to the platinum vessel.‡

With this apparatus the vapour-densities of glucinum chloride and bromide were determined. Glucinum chloride was prepared in several ways, but the best method was found to be that recommended by Nilson, which consists in heating a few mgrms. of the metal in a stream of dry hydrochloric acid in a narrow platinum tube. The chloride is sublimed as near the end of the tube as possible, the connexions removed, and a small cap fitted on the open end. The tube is then cut off with a pair of scissors, so as to form a small capsule inclosing the chloride. This is introduced into a well-corked glass tube and weighed. While the preparation of the chloride was going on, the apparatus was gently heated, and dry carbonic acid passed through it by a glass tube going to the bottom of the platinum vessel, until the issuing gas was completely absorbed by caustic potash.* The glass tube was then gradually withdrawn, and the temperature raised. As soon as the temperature had become constant, which was easily seen by the mercury remaining stationary in both tubes and the resistance of the pyrometer being constant, the cork at the top of the vessel was removed for an instant, the small platinum tube with the substance dropped in, and the cork immediately replaced. The equilibrium was thus hardly disturbed, and a few minutes afterwards the substance was allowed to fall into the heated vessel.

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* During the progress of this part of my work, I received the account of Nilson and Pettersson's experiments on the vapour-density of glucinum chloride ("Berlin Ber.," xvii, 987). It will be observed from the sequel that I have adopted some details from them, notably the use of carbonic acid for displacement.

† " "Berlin Ber.," xiii, 851.

‡ For a description of the construction and graduation of this instrument, see Appendix B.

In the two following determinations (the only ones which were made) evaporation commenced at once, and was complete in about twenty seconds. The following are the data of these two experiments:—

Exp.	Substance.	Displaced CO_2.	*t*.	*d*.
1	26·4 mgrms.	7·47 c.c.	635°	2·733
2	28·0 ,,	7·98 ,,	785	2·714
			Mean	2·724

After each experiment the platinum vessel was washed out with a mixture of potassium iodide and starch, but no trace of free chlorine was found. The small platinum tube was then washed with water, dried, and weighed; this gave the weight of the substance used.

The vapour-density of glucinum bromide was next determined in the same apparatus. This substance can be obtained like the chloride, by heating the metal in dry hydrobromic acid, but, owing to the difficulty of obtaining a regular stream of the dry gas, it is best prepared by burning the metal in gaseous bromine. Combination between the two elements takes place at a low red heat, with brilliant incandescence. The crude bromide is afterwards purified by resubliming it in a current of hydrogen or carbonic acid. Like the chloride, it can be sublimed unchanged in carbonic acid. Glucinum bromide sublimes at a lower temperature than the chloride, and, unlike the latter compound, vaporises before it melts. It begins to volatilise at about 450°. When carefully sublimed at a low temperature, it forms beautiful snow-white silky needles, and does not attack glass if air and moisture are perfectly absent. If heated in the presence of air, free bromine is at once produced.

A quantity of the crude substance was prepared by heating a few centigrams of metallic glucinum in bromine vapour. This was purified by sublimation in dry hydrogen, and was finally sublimed into several narrow glass tubes, each of which was sealed up. When a determination was to be made, the two ends of one of these tubes were cut off, and the solid lump of the bromide quickly rammed into a small platinum tube closed at one end. A cap was fitted on this tube, and it was weighed in the same manner as the chloride.

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* There was always a minute bubble of air left unabsorbed by the potash, even when the gas was passed through the apparatus for 20 hours. It was probably due to diffusion through the caoutchouc connexions, and did not appear to influence the results.

The vapour-density was determined like that of the chloride, and the following are the data of the four experiments made:—

Expt.	Substance.	Volume of CO_2.	*t.*	*d.*
1	—	—	440°	evaporation very slow.
2	35·9 mgrms.	4·28 c.c.	608	6·487
3	61·1 „	7·53 „	630	6·276
4	26·0 „	3·22 „	606	6·245
			Mean	6·336

In these experiments there was always a trace of free bromine produced. In experiment 4, where it was largest, the iodine, set free on the addition of potassium iodide, was estimated by centinormal potassium arsenite, of which 0·2 c.c. was required. This corresponds to 0·16 mgrm. bromine, or less than 1 per cent. of the quantity present. The decomposition which had taken place could not, therefore, affect the result to any appreciable extent, and that the substance had completely evaporated was proved by the fact that the small platinum tube weighed the same before and after the experiment within one or two tenths of a milligram.

The possible densities for glucinum chloride and bromide are—

For $Gl''Cl_2$...... 2·76 For $Gl'''Cl_3$...... 4·14, and
„ $Gl''Br_2$ .... 5·84 „ $Gl'''Br_3$ .... 8·76

The values found were—

For $GlCl_2$ ...... 2·72, and for $GlBr_2$ ...... 6·34.

It is therefore evident that the molecules of these two substances in the gaseous state are represented by the formulæ $GlCl_2$ and $GlBr_2$ respectively, in which the metal is a dyad, and has the atomic weight 9·1. Thus from Avogadro's law, to which there are no known exceptions, the conclusion is confirmed which was obtained from the specific heat of the element at high temperatures.

The long disputed question of the atomic weight of glucinum is thus definitely and finally decided in favour of that number which satisfies the requirements of the periodic law, and another element is added to the long list of those whose atomic weights have been corrected by this important generalisation. In all future determinations of the atomic weight of an element, the position which the element should occupy in the periodic arrangement must receive due importance, and had I fully recognised this two years ago, I should perhaps have stated my conclusions and criticisms less positively than I did.

Appendix A.

On the Composition of the Double Carbonate of Glucinum and Ammonium.

An analysis of this important compound has been published by Debray,* but the formula he obtained being somewhat complex, I have prepared and analysed the pure substance. A strong solution of ammonium carbonate was digested with moist glucinum carbonate at a gentle heat until saturated. The clear solution was then heated until it became cloudy, and any excess of ammonium carbonate decomposed, then again filtered and mixed with its own bulk of strong alcohol. The crystals, which only separated slowly and adhered firmly to the walls of the containing vessel, were drained, washed with alcohol, and dried between filter-paper.

The analyses of two separate specimens gave the following results :—

	I.	II.	Mean.	Calculated.
BeO	18·77	19·22	19·00	18·40
CO_2	42·13	43·16	42·65	43·00
$(NH_4)_2O$	26·39	26·25	26·31	25·41
H_2O (diff.) ..	12·71	11·37	12·04	13·19
	100·00	100·00	100·00	100·00

which correspond to the formula $2(GlCO_3,Am_2CO_3),Gl(OH)_2+2H_2O$. This resembles the formula obtained by Debray, viz.,

$$3(GlCO_3,Am_2CO_3),Gl(OH)_2,$$

but contains more water. Both of my specimens were dry crystalline powders, without a trace of adhering alcohol, and with a faint odour of ammonia. Specimen II had been kept for several weeks in a stoppered bottle.

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* "Ann. d. Chim." [3], xliv, 5.

APPENDIX B.

Note on Siemens' Pyrometer.

The following are the details of construction and graduation of the pyrometer employed in the vapour-density determinations. About 100 cm. of thin platinum wire (0·13 mm. diameter) was coiled round a thick piece of ordinary clay tobacco-pipe, and three thicker platinum wires were soldered with gold to the two ends. To these thicker wires were soldered three copper wires, which went to the bridge where the resistance was measured. The whole was enclosed in a porcelain tube, one end of which had been closed by a plug of clay, and the wires were so arranged that the junctions between the copper and platinum came at the same height, just within the tube. By suitably arranging the three wires and a known resistance in the arms of the bridge, measurements could be made of the resistance of the thin coil without that of the leads, so that any change in resistance was due to the altered resistance of the coil alone. The wire of which the coil was made had previously been heated several times to redness.

In order to graduate the instrument it was immersed in melting ice, boiling water, aniline, diphenylamine, sulphur, selenium, and zinc. For boiling these substances (with the exception of water) iron tubes welded together at one end, of 5 cm. diameter and 46 cm. length, were used. The upper portion of the tube for about 8 cm. was surrounded with a coil of thin lead tubing, through which a stream of cold water was allowed to flow. This acted as a very efficient condenser, and kept the upper part of the tube cool enough to handle easily. The results obtained are expressed in the following table, in which the first column gives the substance, the second its melting or boiling point, and the third the actual resistance found. In the fourth column the resistances are reduced to that at 0°=1, and in the fifth are given the corresponding resistances, calculated from the empirical formula—

$$r_t = 1 + 0{\cdot}0027t - 0{\cdot}00000019t^2.$$

Substance.	t.	r_t.	$r_0 = 1$.	Calculated.
Ice	0°	13·42	1·000	1·000
Water	100	17·02	1·268	1·268
Aniline	184	20·08	1·496	1·493
Diphenylamine	310	24·43	1·819	1·819
Sulphur	448	29·14	2·171	2·172
Selenium	665	36·08	2·688	2·712
Zinc	940	45·38	3·381	3·370

The agreement between the calculated and observed results is good, except in the last two instances. The selenium probably contained some sulphur, which would lower its boiling point, and only one experiment was made with zinc, as this temperature could only be reached in the furnace used under an exceptionally favourable gas pressure.

The change in the resistance of commercial platinum has been investigated by the late Sir W. Siemens, M. Benoit, and others.

Siemens expressed his results in the form—

$$r_t = r_o(\mathrm{A}\mathrm{T}^{\frac{1}{2}} + \mathrm{BT} - \mathrm{C}),$$

and this can be thrown into a general expression similar to that which I have used, viz.:—

$$r_t = r_o(1 + \alpha t - \beta t^2).$$

Benoit's results* can also be expressed by a similar formula.

But although there is a general agreement between these different results, the values of the coefficients vary considerably, and it is therefore always necessary in using this pyrometer to calibrate it for every wire. I have even found that the change of resistance of two pieces of wire from the same bobbin varied considerably.

M. Benoit has kindly furnished me with the following synopsis of various results, which, although they differ much from one another, can all be expressed by the general formula given above:—

	Siemens.					
t.	I.	II.	III.	Benoit.	Erhardt.†	Humpidge.
0° ..	1·00	1·00	1·00	1·00	1·00	1·00
100 ..	1·29	1·25	1·31	1·23	1·23	1·27
200 ..	1·47	1·50	1·62	1·46	1·46	1·53
400 ..	1·84	1·98	2·23	1·91	1·90	2·05
600 ..	2·16	2·48	2·81	2·34	2·31	2·55
800 ..	2·43	2·97	3·37	2·75	2·69	3·04

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* *Compt. rend.*, lxxvi, 342. The formula is incorrectly given in Wiedemann's "Electricität," the sign of second coefficient being positive instead of negative. One of the temperatures used in this research was that of boiling cadmium, which was taken from the earlier and incorrect determinations (with an iodine thermometer) of Deville and Troost as 860° instead of *circâ* 770°. M. Benoit has, however, informed me, in a private communication, that on introducing this correction the general form of the equation remains the same.

† "Wied. Ann." xxiv, 215.

APPENDIX C.

Details of Specific Heat Determinations.

I. *Specific Heat of Turpentine.*

(i.) *By Method of Mixture with Magnesium.*

(*a*.) *Specific Heat of Magnesium.*

w=weight of substance, w'=weight of platinum wire as support, W=weight of water; water-equivalent of calorimeter, agitator, and thermometer=2·84, T=temperature of substance, t=initial temperature of liquid, θ=final temperature of mixture, c=calculated specific heat. [Specific heat of water at $t°=1+0·0003t$.]

Expt. 1.. $w = 4·739$, $w' = 0·156$, $W = 85·21$,
$T = 99°·61$, $\theta = 12°·57$, $t = 11°·41$
$\therefore c_1 = 0·2474$.

Expt. 2.. $W = 85·22$, $T = 99°·96$, $\theta = 11°·38$, $t = 10°·21$
$\therefore c_2 = 0·2452$.

Expt. 3.. $W = 85·22$, $T = 98°·80$, $\theta = 12°·79$, $t = 11°·65$
$\therefore c_3 = 0·2428$.

Expt. 4.. $W = 85·22$, $T = 98°·78$, $\theta = 13°·78$, $t = 12°·66$
$\therefore c_4 = 0·2412$.

Mean: $c_{14}^{100} = 0·2442$.

(*b*.) *Specific Heat of Turpentine.*

w and w' as before. W=weight of turpentine, equivalent of calorimeter, &c.=2·83.

Expt. 1.. $W = 75·80$, $T = 98°·20$, $\theta = 14°·57$, $t = 11°·67$,
$\therefore c_1 = 0·4111$.

Expt. 2.. $W = 75·17$, $T = 99°·54$, $\theta = 15°·27$, $t = 12°·47$,
$\therefore c_2 = 0·4274$.

Expt. 3.. $W = 75·12$, $T = 98°·20$, $\theta = 14°·60$, $t = 11°·74$,
$\therefore c_3 = 0·4206$.

Expt. 4.. $W = 75·43$, $T = 97°·95$, $\theta = 12°·97$, $t = 10°·03$,
$\therefore c_4 = 0·4140$.

Expt. 5.. $W = 75·02$, $T = 97°·98$, $\theta = 13°·58$, $t = 10°·64$,
$\therefore c_5 = 0·4131$.

Expt. 6.. $W = 75{\cdot}09$, $T = 99^\circ{\cdot}26$, $\theta = 14^\circ{\cdot}50$, $t = 11^\circ{\cdot}62$,
$\therefore c_6 = 0{\cdot}4174$.

Expt. 7.. $W = 76{\cdot}24$, $T = 99^\circ{\cdot}50$, $\theta = 15^\circ{\cdot}09$, $t = 12^\circ{\cdot}28$,
$\therefore c_7 = 0{\cdot}4210$.

Mean : $c_{10}^{15\cdot3} = k_{12\cdot7} = 0{\cdot}4179$,
and $k_{10} = 0{\cdot}4146$.

(ii.) *By Andrews' Calorifer.*

Equivalent of calorimeter and thermometer $=10{\cdot}33$, weight of water $=262{\cdot}34$. The mean of five experiments gave $\theta=8^\circ{\cdot}436$, $t=7{\cdot}016^\circ$,
whence equivalent of calorifer =

$$= 272{\cdot}67 \times 1{\cdot}42 = 387{\cdot}19 \div 1{\cdot}0023$$
$$= 386{\cdot}20$$

In two series of experiments, using turpentine instead of water, the following results were obtained:—

Series i.—Weight of turpentine $=229{\cdot}26$,

$$\theta = 12^\circ{\cdot}298,\ t = 8^\circ{\cdot}594 \text{ (5 experiments)}$$
$$\therefore k_{10\cdot5} = 0{\cdot}4107.$$

Series ii.—Weight of turpentine $=229{\cdot}26$,

$$\theta = 12^\circ{\cdot}480,\ t = 8^\circ{\cdot}790 \text{ (4 experiments)}$$
$$\therefore k_{10\cdot5} = 0{\cdot}4115,$$

whence $k_{10} = 0{\cdot}4105$.

(iii.) *By Electrical Method.*

Mean of three experiments gave

$k_{16\cdot2} = 0{\cdot}4180$, compared with water at $14^\circ{\cdot}2$,
whence $k_{10} = 0{\cdot}4085$.

The general mean of the three sets of determinations is

$$k_{10} = 0{\cdot}4112,$$

which was adopted, with a correction for the temperature, in calculating the specific heat of glucinum in the following experiments:—

II. *Specific Heat of Glucinum.*

(i.) *In Turpentine.*

Weight of substance $=0{\cdot}745$, weight of platinum casing $=1{\cdot}527$, water equivalent of calorimeter, &c. $=2{\cdot}83$.

Expt. 1.. $W = 74\cdot98,\ T = 99^\circ\cdot45,\ \theta = 11^\circ\cdot29,\ t = 10^\circ\cdot33,$
$\therefore c_1 = 0\cdot4272.$

Expt. 2.. $W = 74\cdot98,\ T = 99^\circ\cdot36,\ \theta = 11^\circ\cdot08,\ t = 10^\circ\cdot12,$
$\therefore c_2 = 0\cdot4262,$
and $c^{11\cdot2}_{99\cdot4} = 0\cdot4267.$

Expt. 3.. $W = 74\cdot97,\ T = 145^\circ\cdot2,\ \theta = 11^\circ\cdot95,\ t = 10^\circ\cdot44,$
$\therefore c_1 = 0\cdot4481.$

Expt. 4.. $W = 74\cdot97,\ T = 145^\circ\cdot2,\ \theta = 14^\circ\cdot63,\ t = 13^\circ\cdot15,$
$\therefore c_2 = 0\cdot4518,$
and $c^{13\cdot3}_{145\cdot2} = 0\cdot4500.$

Expt. 5.. $W = 74\cdot87,\ T = 190^\circ\cdot1,\ \theta = 10^\circ\cdot08,\ t = 7^\circ\cdot95,$
$\therefore c_1 = 0\cdot4668.$

Expt. 6.. $W = 74\cdot87,\ T = 196^\circ\cdot2,\ \theta = 11^\circ\cdot18,\ t = 8^\circ\cdot99,$
$\therefore c_2 = 0\cdot4684,$
and $c^{10\cdot6}_{193\cdot1} = 0\cdot4676.$

Expt. 7.. $W = 74\cdot97,\ T = 241^\circ\cdot9,\ \theta = 14^\circ\cdot58,\ t = 11^\circ\cdot82,$
$\therefore c_1 = 0\cdot4875.$

Expt. 8.. $W = 74\cdot97,\ T = 236^\circ\cdot2,\ \theta = 16^\circ\cdot23,\ t = 13^\circ\cdot58,$
$\therefore c_2 = 0\cdot4856,$
and $c^{15\cdot4}_{239\cdot0} = 0\cdot4866.$

Expt. 9.. $W = 74\cdot97,\ T = 309^\circ\cdot9,\ \theta = 14^\circ\cdot72,\ t = 10^\circ\cdot99,$
$\therefore c_1 = 0\cdot5093.$

Expt. 10.. $W = 74\cdot70,\ T = 313^\circ\cdot5,\ \theta = 14^\circ\cdot61,\ t = 10^\circ\cdot83,$
$\therefore c_2 = 0\cdot5080,$
and $c^{14\cdot7}_{311\cdot7} = 0\cdot5087.$

(ii.) *In Double Calorimeter.*

Weight of platinum cylinder$=24\cdot346$, $W=$weight of water and equivalent of calorimeter, &c. I (for platinum), $W'=$weight of water and equivalent of calorimeter II (for glucinum).

Expt. 11. $W = 95\cdot15,\ \theta = 12^\circ\cdot52,\ t = 9^\circ\cdot53,$
whence $T = 359\cdot3^\circ.$
$W' = 93\cdot86,\ \theta' = 11^\circ\cdot72,\ t' = 10^\circ\cdot11,$
and $c^{11\cdot7}_{359\cdot3} = 0\cdot5178.$

Expt. 12. $W = 96\cdot19,\ \theta = 18^\circ\cdot60,\ t = 14^\circ\cdot88,$
whence $T = 447^\circ\cdot1.$
$W' = 95\cdot74,\ \theta' = 17^\circ\cdot52,\ t' = 15^\circ\cdot50$
and $c^{17\cdot5}_{447\cdot1} = 0\cdot5384.$

FIG. 1.

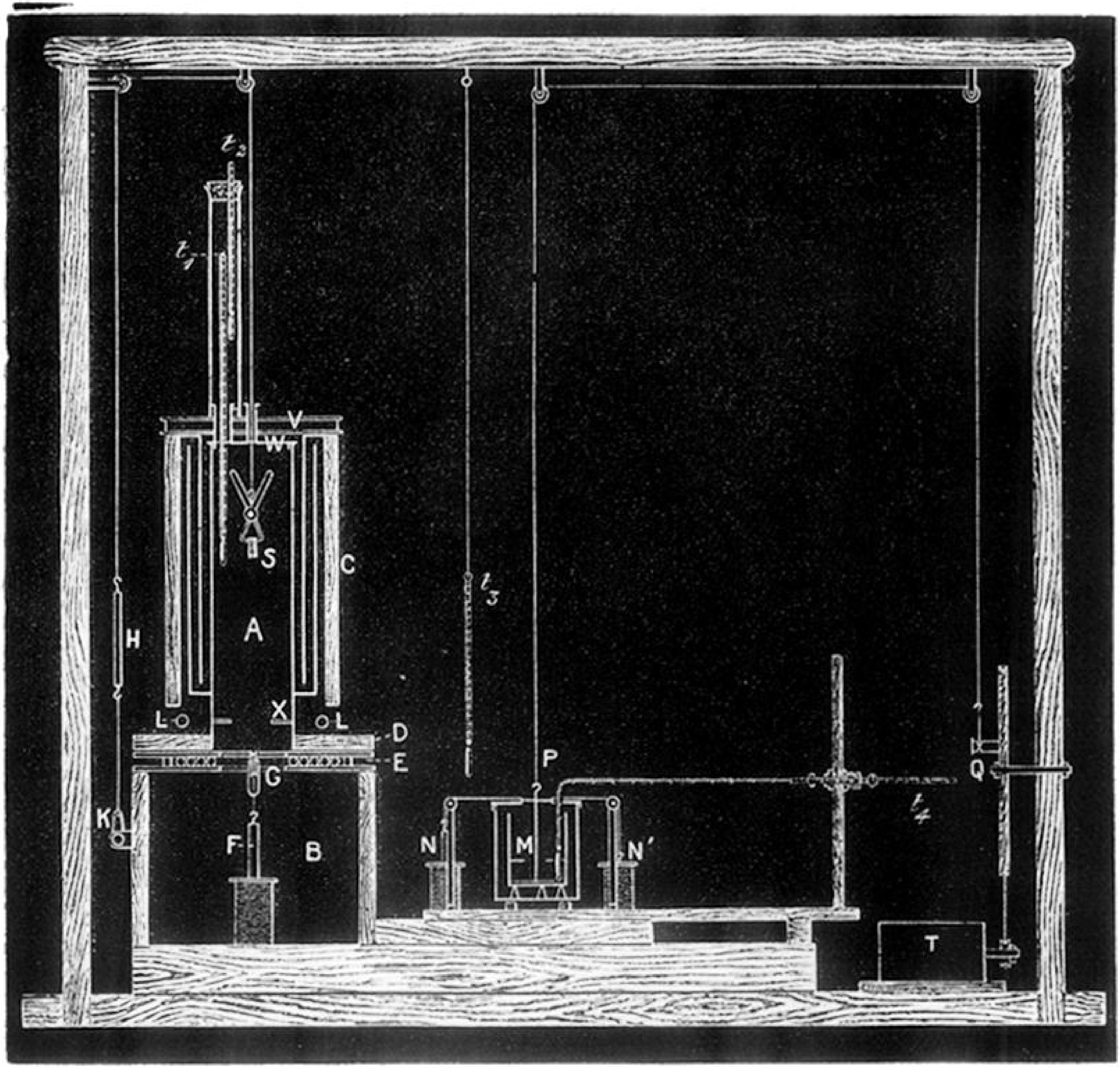


Fig. 2.

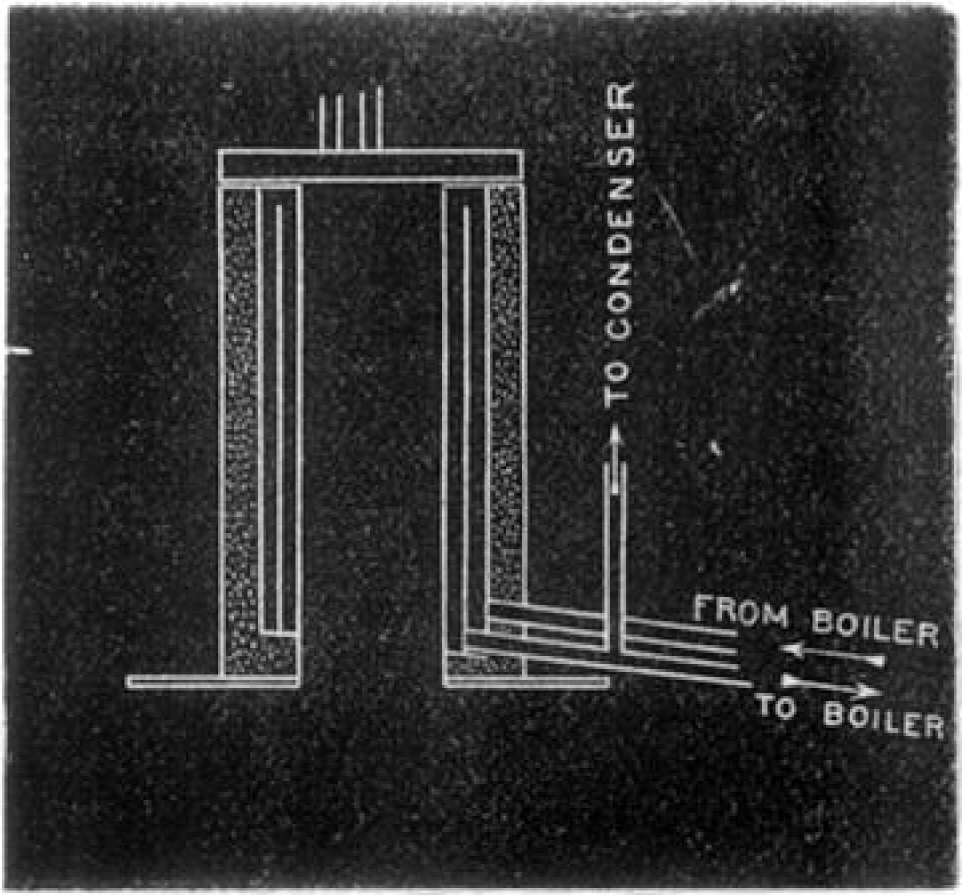
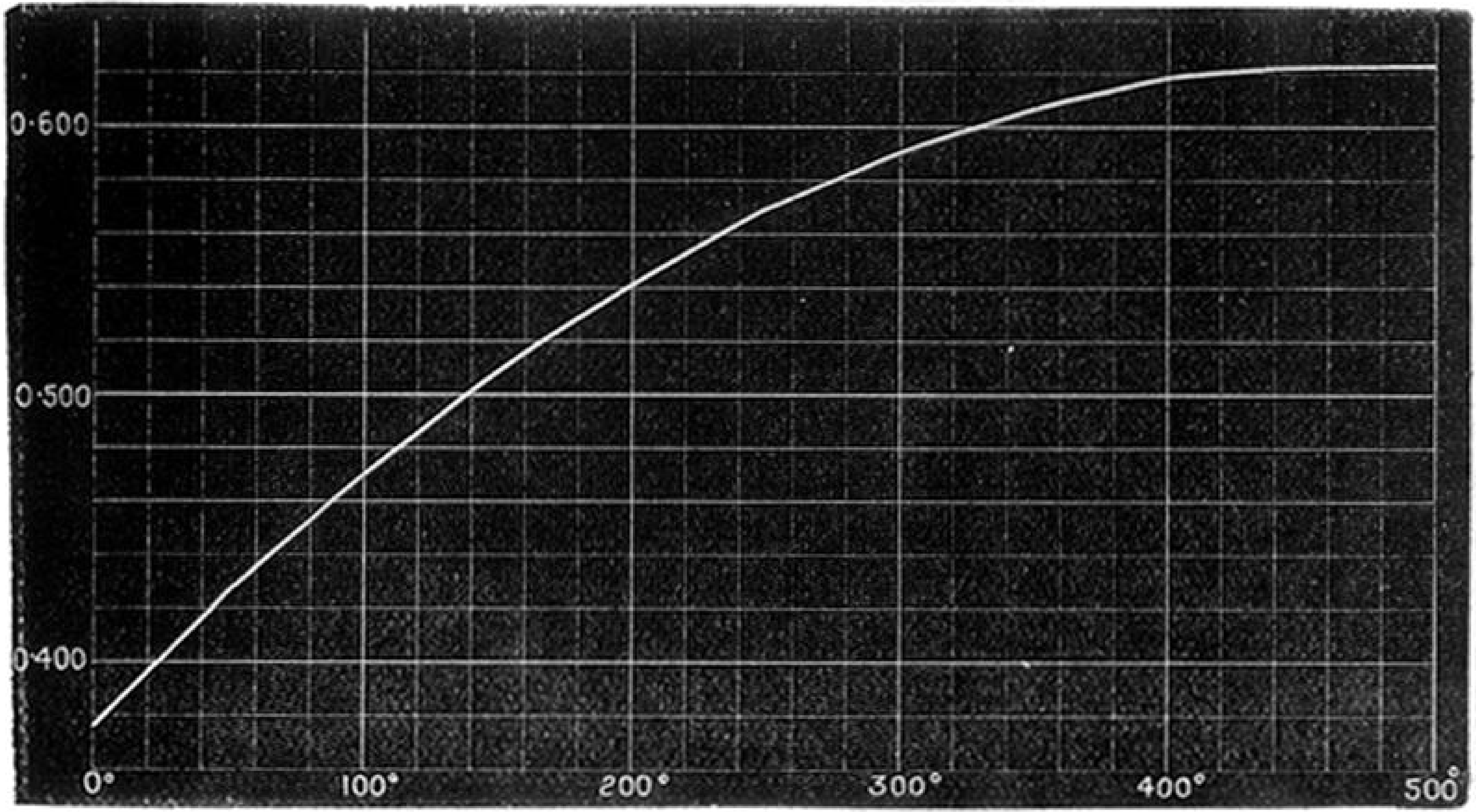


FIG. 3.



Curve showing specific heat of glucinum at varying temperatures.